Tannins and Related Compounds. LXXVII.[1] Novel Chalcan-flavan Dimers, Assamicains A, B and C, and a New Flavan-3-ol and Proanthocyanidins from the Fresh Leaves of *Camellia sinensis* L. var. *assamica* KITAMURA

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Three novel chalcan-flavan dimers, assamicains A (1), B (2) and C (3), and a new flavan-3-ol (14) and proanthocyanidins (19, 20) have been isolated, together with the known flavan-3-ols (4—13), proanthocyanidins (15—18, 21), theasinensins (22—24) and hydrolyzable tannins (25, 26), from the fresh leaves of *Camellia sinensis* var. *assamica* (Camelliaceae), and their structures have been established on the basis of spectroscopic evidence in conjunction with thiolytic degradation and enzymatic hydrolysis.

Keywords *Camellia sinensis* var. *assamica*; Camelliaceae; polyphenol; assamicain; chalcan-flavan dimer; proanthocyanidin; theasinensin; flavan-3-ol; hydrolyzable tannin; black tea

As part of our chemical examinations of polyphenolic constituents in various beverage teas, we previously reported the isolation and structural elucidation of several types of compounds such as hydrolyzable tannins,[2] acylated flavan-3-ols,[3,4] proanthocyanidins,[3] B,B′-linked bisflavanoids[3,5] and benzotropolone-type red pigments[6] from green tea, oolong tea and black tea. During these studies, considerable qualitative and quantitative variations of the polyphenols were found among these teas. In particular, the phenolic patterns of the green tea (non-fermented) and black tea (fermented) differed markedly, the latter characteristically containing unique compounds formed by endogeneous polyphenol oxidase during fermentation. We have therefore extended our work to the fresh material (*Camellia sinensis* var. *assamica*) of the black tea; this has resulted in the isolation and characterization of novel chalcan-flavan dimers named assamicains A (**1**), B (**2**) and C (**3**), and a new flavan-3-ol derivative (**14**) and pro-

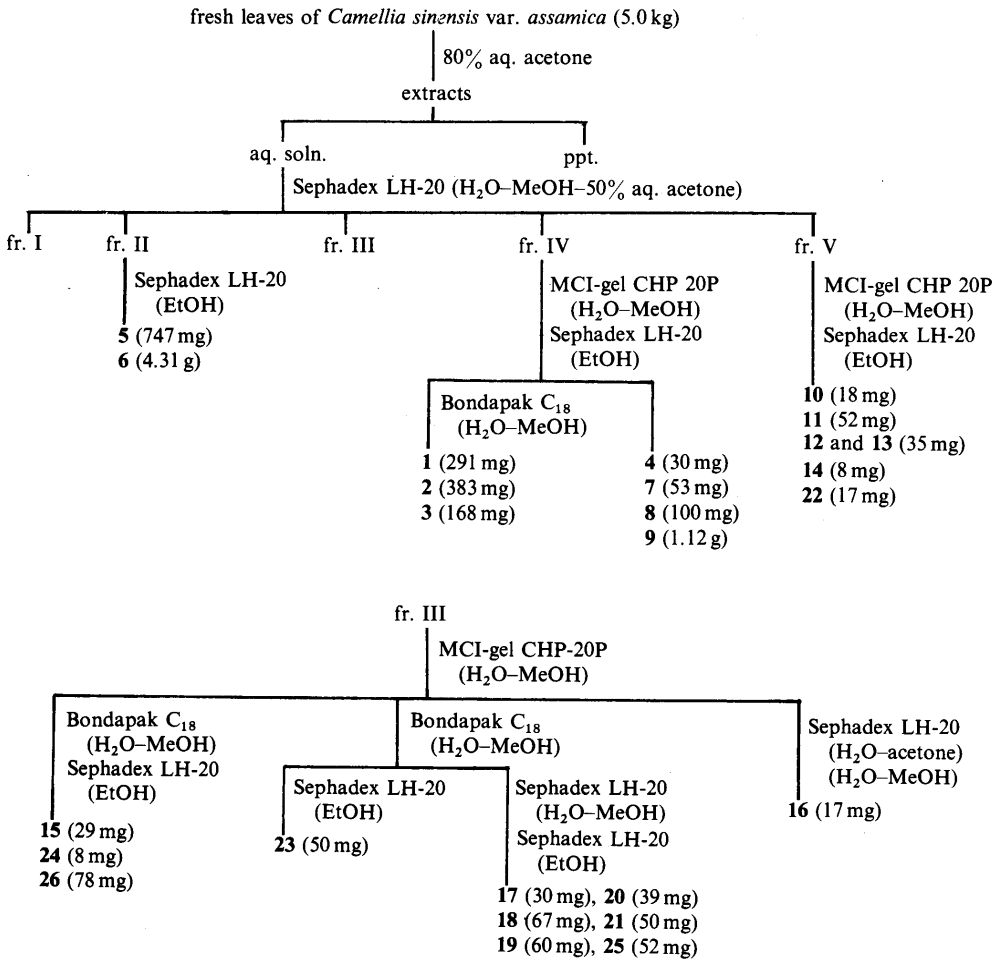
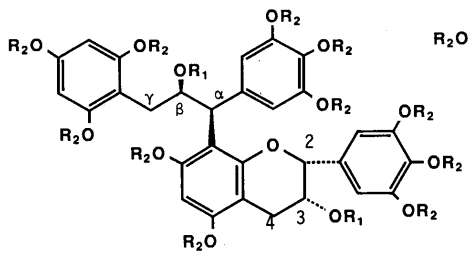


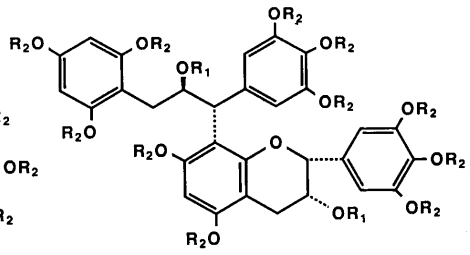
Chart 1

anthocyanidins (**19**, **20**), together with the known flavan-3-ols (**4**—**13**), proanthocyanidins (**15**—**18**, **21**), theasinensins (**22**—**24**) and hydrolyzable tannins (**25**, **26**). We now wish to give a detailed account of the structures of these compounds.

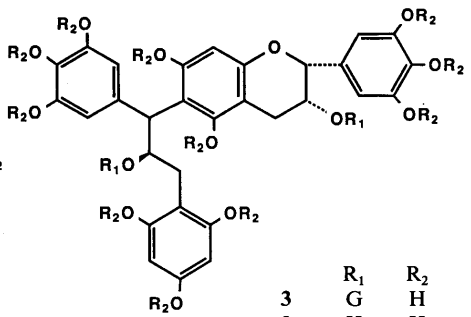
The extraction and isolation procedures are summarized in Chart 1. Among the twenty-six polyphenols isolated here, compounds **4**—**13**, **15**—**18** and **21**—**26** were found to be identical with (−)-epiafzelechin (**4**),[7] (−)-epicatechin (**5**),[7] (−)-epigallocatechin (**6**),[8] (−)-epiafzelechin 3-*O*-gallate (**7**),[4] (−)-epicatechin 3-*O*-gallate (**8**),[8] (−)-epigallocatechin 3-*O*-gallate (**9**),[8] (−)-epicatechin 3,5-di-*O*-gallate (**10**),[4] (−)-epigallocatechin 3,5-di-*O*-gallate (**11**),[3] (−)-epigallocatechin 3,3′- and 3,4′-di-*O*-gallate (**12**, **13**),[3] procyanidins B-2 (**15**),[2] C-1 (**16**),[2] B-3 (**17**)[9] and B-4 (**18**),[2] prodelphinidin B-4 (**21**),[10] theasinensins A (**22**) and B



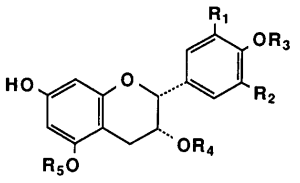
	R_1	R_2
1	G	H
1a	H	H
1b	H	Me
1c	G(Me)	Me



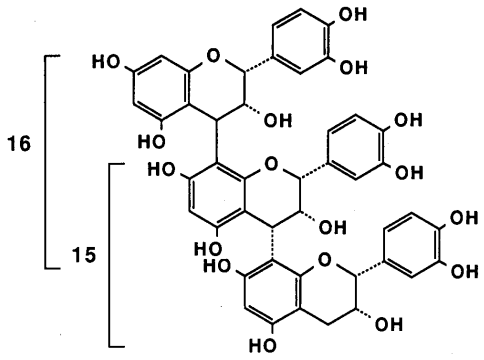
	R_1	R_2
2	G	H
2a	H	H
2b	H	Me
2c	G(Me)	Me

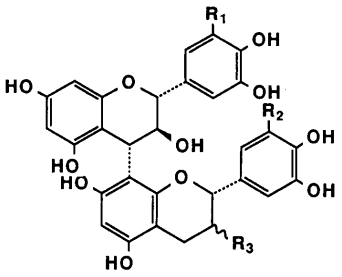


	R_1	R_2
3	G	H
3a	H	H
3b	H	Me

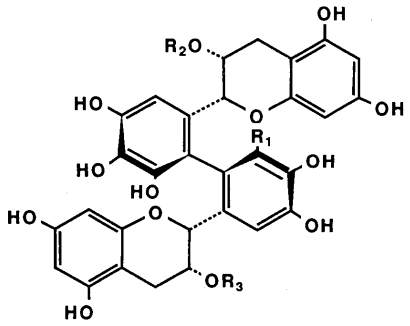


	R_1	R_2	R_3	R_4	R_5
4	H	H	H	H	H
5	OH	H	H	H	H
6	OH	OH	H	H	H
7	H	H	H	G	H
8	OH	H	H	G	H
9	OH	OH	H	G	H
10	OH	H	H	G	G
11	OH	OH	H	G	G
12	OH	OG	H	G	H
13	OH	OH	G	G	H
14	OH	OH	H	caffeoyl	H

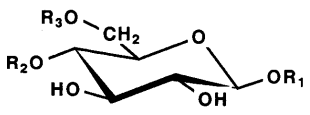




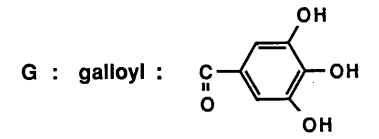
	R_1	R_2	R_3
17	H	H	◄OH
18	H	H	····OH
19	H	OH	····OH
20	OH	H	····OH
21	OH	OH	····OH

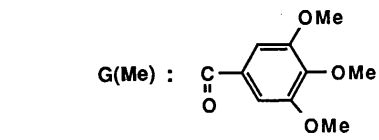


	R_1	R_2	R_3
22	OH	G	G
23	OH	H	G
24	H	H	H



	R_1	R_2	R_3
25	G	G	G
26	G	HHDP	





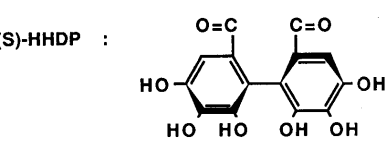


Chart 2

(**23**),[3] desgalloyl theasinensin F (**24**),[5] 1,4,6-tri-*O*-galloyl-*β*-D-glucopyranose (**25**)[2] and 1-*O*-galloyl-4,6-(*S*)-hexahydroxydiphenoyl-*β*-D-glucopyranose (**26**)[2] (Chart 2).

Assamicain A (**1**) showed a dark blue coloration with the ferric chloride reagent and an orange coloration with the anisaldehyde–sulfuric acid reagent,[11] suggesting the presence of a pyrogallol ring and a flavan-3-ol moiety in the molecule. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum (Table I) of **1** exhibited a two-proton multiplet at δ 2.76—3.02, a one-proton broad singlet at δ 5.02 and a one-proton multiplet at δ 5.48, which were attributable to the protons of the flavan C-4, C-2 and C-3, respectively. In addition, the appearance of a two-proton singlet at δ 6.72 arising from the flavan B-ring and of a one-proton singlet at δ 6.06 from the A-ring suggested the presence of an epigallocatechin moiety with a substituent in the C-6 or C-8 position. The aliphatic signals at δ 3.02—3.05 (2H, m) and δ 5.01 (1H, d, J=16 Hz), which were correlated with the carbon-13 nuclear magnetic resonance (^{13}C-NMR) signals at δ 28.8 and 45.7, respectively, were assignable to a benzylic methylene and a methine having no oxygen function, while the resonance at δ 5.48 was similarly attributed to an oxygen-bearing methine. In the aromatic region, two two-proton signals appeared as singlets at δ 5.82 and 6.49, the chemical shifts and the coupling patterns being consistent with the presence of symmetrical phloroglucinol and pyrogallol rings, respectively. These ^{1}H- and ^{13}C-NMR observations suggested that **1** possesses a chalcan-*β*-ol unit connected to an epigallocatechin moiety through a carbon–carbon linkage. In addition, the appearance of two galloyl signals at δ 6.95 (overlapped, 4H) and the lowfield shifts of the above-mentioned H-3 signal in

Table I. ^{1}H-NMR Spectral Data for Assamicains[a]

	1	2	3	32	1a	2a	3a
Chalcan unit							
α-H	5.01 (br d, J=6 Hz)	4.87 (d, J=10 Hz)	5.07 (d, J=6 Hz)	4.79 (d, J=10 Hz)	4.84 (br d, J=5 Hz)	4.48 (d, J=8 Hz)	4.83 (d, J=4 Hz)
β-H	6.56 (m)	—[b]	6.48 (m)	6.63 (m)	4.64—4.92 (m)	4.76—5.08 (m)	4.56—4.76 (m)
γ-H	3.02—3.50 (m)	2.76—3.24 (m)	2.76—3.31 (m)	2.82—3.12 (m)	2.67 (dd, J=14, 8 Hz) 3.13 (d, J=14 Hz)	2.57 (dd, J=14, 9 Hz) 3.12 (d, J=14 Hz)	2.64 (dd, J=14, 10 Hz) 2.99 (dd, J=14, 2 Hz)
2,6-H	6.49 (s)	6.80 (s)	6.55 (s)	6.66 (s)	6.37 (s)	6.64 (s)	6.41 (s)
3′,5′-H	5.82 (s)	5.80 (s)	5.83 (s)	5.81 (s)	6.00 (s)	5.92 (s)	6.00 (s)
Flavan unit							
2-H	5.02 (br s)	5.15 (br s)	4.96 (s)	4.99 (s)	4.76 (s)	4.81 (s)	4.79 (s)
3-H	5.48 (m)	5.55 (m)	5.51 (m)	5.49 (m)	4.20 (m)	4.26 (m)	4.20 (m)
4-H	2.76—3.02 (m)	2.76—3.24 (m)	2.76—3.31 (m)	2.82—3.12 (m)	2.80—2.97 (m)	2.75—2.96 (m)	2.80—2.90 (m)
6-H	6.06 (br s)	6.13 (s)	—	—	6.10 (s)	6.14 (s)	—
8-H	—	—	6.16 (s)	6.24 (s)	—	—	6.06 (s)
2′,6′-H	6.72 (s)	6.90 (s)	6.67 (s)	6.70 (s)	6.60 (s)	6.65 (s)	6.62 (s)
Galloyl							
2,6-H	6.95 (4H) (s)	6.95 (s), 7.03 (s)	6.94 (s), 7.05 (s)	6.99 (s), 7.02 (s)	—	—	—

a) Measured in acetone-d_6 + D_2O at 100 MHz. b) Overlapped with aromatic signals.

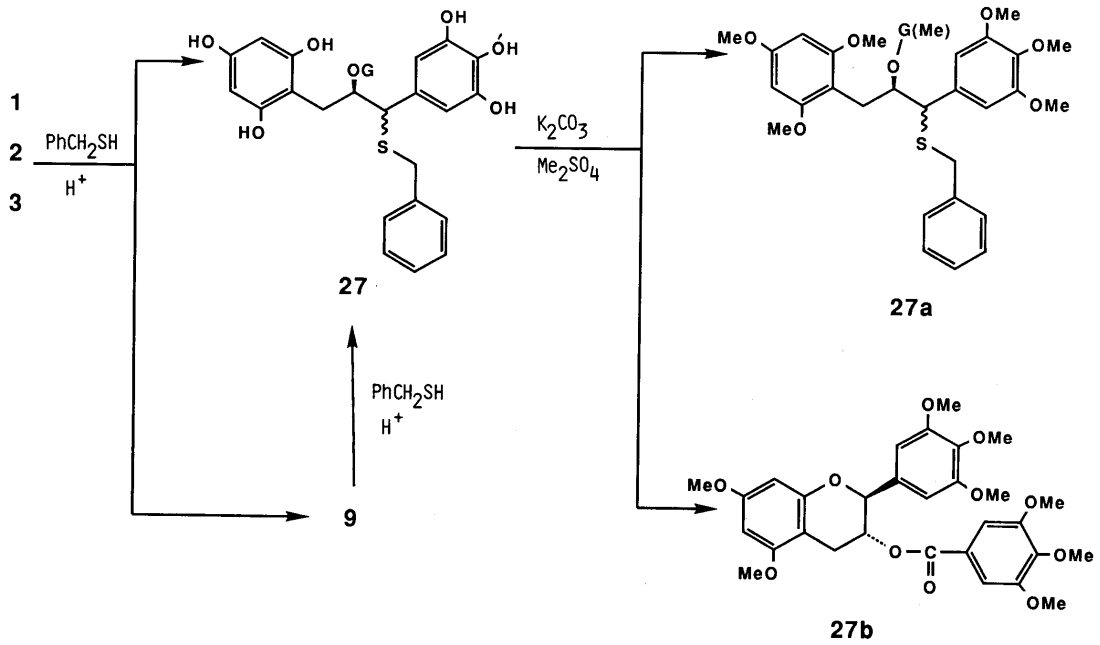


Chart 3

TABLE II. ^{13}C-NMR Spectral Data for Assamicains and Their Derivatives[a]

	1	2	3	1a	2a	3a	1b	2b	3b	28	29
Chalcan unit											
α-C	45.7	46.7	45.3	46.1	48.7	46.1	49.6	48.8	49.3	46.9	46.6
β-C	75.2	75.1	76.3	76.8	75.8	71.4	73.0	72.7	72.3	75.5	74.7
γ-C	28.8[b]	28.0[b]	29.4[b]	30.2[b]	30.4[b]	29.6[b]	29.1[b]	29.4	28.7[b]	28.7	27.3
1-C	130.9	131.0	131.6	131.4	131.6	131.4	139.3	138.9	138.9	138.1	138.7
2,6-C	110.1	110.1	108.5	108.4	110.1	108.3	105.9	105.8	106.7	106.7	106.9
3,5-C	145.3[c]	144.9[c]	145.4[c]	145.8[c]	145.5[c]	146.0	152.5[c]	152.4[b]	152.3[c]	152.2[b]	152.2[b]
4-C	131.7	133.2	133.2	134.9	135.1	134.6	139.3	138.9	138.9	137.9	137.9
1′-C	104.1	103.4	103.6	105.8	105.8	105.4	108.8	109.6	105.0	107.4	105.4
2′,6′-C	157.5	157.7	157.7	157.8	157.7	157.4	159.0	159.1	159.1	159.1	159.4
3′,5′-C	95.3	95.3	95.1	96.1	96.1	95.7	90.8	92.0	90.8	90.1	90.2
4′-C	156.6	156.9	156.9	157.2	157.3	157.4	159.5	159.7	159.7	159.6	159.6
Flavan unit											
2-C	78.0	78.6	77.9	79.4	79.6	79.2	78.7	79.1	78.6	77.7	78.0
3-C	70.3	70.3	70.0	66.7	66.6	66.9	66.1	66.8	66.5	68.4	68.2
4-C	26.8[b]	27.1[b]	27.2[b]	29.4[b]	29.5[b]	29.1[b]	29.7[b]	29.4	29.9[b]	26.5	25.6
4a-C	99.3	99.4	100.0	99.5	100.1	100.7	101.2	101.2	108.6	100.4	100.8
6-C	96.5	97.3	109.0	97.4	97.3	107.7	89.5	89.3	118.3	88.5	88.4
8-C	110.1	110.1	96.7	107.1	110.9	95.7	111.2	112.2	96.8	111.3	110.5
5,7,8a-C	154.7	154.3	154.8	154.9	154.3	155.0	156.7	156.6	157.7	156.7	157.1
	154.9	154.7	155.3	155.5	154.5	155.7	157.0	157.5	158.1	156.9	
		155.1	155.8	155.8	155.2	156.0	157.3				
1′-C	130.9	131.6	130.4	131.4	131.4	131.4	134.0	134.6	133.9	133.6	133.6
2′,6′-C	107.2	107.1	106.6	107.1	107.1	106.9	103.7	103.3	103.4	104.4	104.1
3′,5′-C	145.3[c]	145.3[c]	145.7[c]	146.0[c]	145.8[c]	146.0	153.3[c]	153.3[b]	153.5[c]	152.5[b]	152.5[b]
4′-C	132.7	135.8	132.9	132.7	132.9	134.6	136.0	135.5	136.3	136.0	136.3
Galloyl											
–COO–	166.7	166.8	166.3	—	—	—	—	—	—	165.0	165.3
	167.1	167.2	166.8							166.0	(2C)
1-C	121.1	121.3	121.3	—	—	—	—	—	—	124.8	124.9
	122.4	122.6	121.9							126.8	126.7
2,6-C	110.1	110.1	110.0	—	—	—	—	—	—	106.2	106.6
	(4C)	(4C)	(4C)							(4C)	(4C)
3,5-C	145.5[c]	145.6[c]	146.0	—	—	—	—	—	—	152.9[b]	152.9[b]
	(4C)	146.0[c]	(4C)							153.1[b]	153.2[b]
4-C	139.1	138.1	138.4	—	—	—	—	—	—	141.2	141.5
	(2C)	139.0	138.9							142.4	142.5
OCH_3							55.3	55.2	55.3	55.2	55.2
							55.5	55.4	55.6	55.4	55.3
							56.1	55.9	56.2	55.7	55.6
							60.7	56.3	60.5	55.9	56.0
								56.5	60.9	56.1	56.2
								60.5		60.6	60.5
								60.7		60.8	60.8

a) Measured in acetone-d_6 + D_2O at 25.05 MHz. *b*, *c*) Signals may be interchanged in each column.

the epigallocatechin moiety and the β-methine signal in the chalcan unit implied the presence of galloyl groups at these positions.

Thiolytic degradation of **1** with benzylmercaptan in the presence of hydrochloric acid[11] yielded a benzylthioether (**27**) and (−)-epigallocatechin 3-*O*-gallate (**9**). On subsequent methylation with dimethyl sulfate and potassium carbonate in dry acetone, the thioether (**27**) afforded unexpectedly the (−)-gallocatechin octamethyl ether (**27b**),[12] together with the nonamethyl ether (**27a**) of the thioether. The formation of **27b** seemed to be unusual, but thereby the absolute configuration of the β-methine carbon could be determined unequivocally to be in the *R*-series.

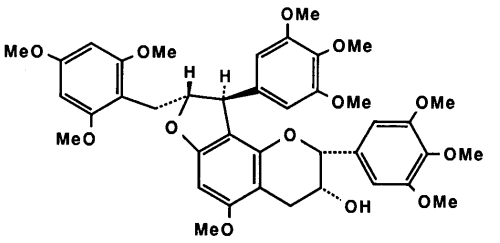
The configuration of the α-methine carbon was determined as follows. Enzymatic hydrolysis of **1** with tannase afforded gallic acid and a hydrolysate (**1a**), which was successively methylated in the same way as described above to give the corresponding undecamethyl ether (**1b**). When treated with *p*-toluenesulfonic acid in dry benzene,[13] **1b** readily released methanol to give a dihydrobenzofuran derivative (**28**). The dihydrobenzofuran structure of **28** followed from the electron-impact mass spectrum (EI-MS), which exhibited the M^+ peak at *m/z* 734, together with prominent fragment peaks at *m/z* 552, 343 (base peak) and 181 originated from the fission of the β,γ-linkage and a retro-Diels–Alder-type cleavage of the flavan C-ring (Chart 5). The ^{1}H-NMR spectrum of **28** showed the α-methine signal at δ 4.39 with a coupling constant of 3.9 Hz, from which the dihedral angle between the α- and β-protons was calculated to be *ca.* 130° (Fig. 1), thus suggesting the *S*-configuration of the α-carbon. Further support for the *S*-configuration was obtained by circular dichroism (CD) analysis of **28**, which exhibited a strong positive Cotton effect at 248 nm (Fig. 1). Application of the aromatic quadrant rule indicated that only the case when the chalcan aromatic ring is located in the upper left makes the positive contribution to the 248 nm Cotton effect.

The ^{13}C-NMR spectrum of the undecamethyl ether (**1b**)

showed flavan C-6, C-8 and C-4a signals at δ 89.5, 111.2 and 102.2, respectively, the chemical shifts being in good agreement with those of the C-8 substituted gambiriin A_1 nonamethyl ether (**30**)[13] [δ 88.6 (C-6), 112.2 (C-8) and 102.5 (C-4a)] rather than the alternative C-6 substituted gambiriin A_3 nonamethyl ether (**31**) [δ 117.7 (C-6), 96.1 (C-8) and 108.4 (C-4a)]. From these findings, the chalcan unit was concluded to be attached to the C-8 position of the epigallocatechin moiety.

Assamicain B (**2**) exhibited, in the fast atom bombardment mass spectrum (FAB-MS), the same $(M+H)^+$ peak at *m/z* 917 as that of **1**. The presence of a 3-*O*-galloyl epigallocatechin moiety and a chalcan unit was readily seen from the ^{1}H- and ^{13}C-NMR spectra (Tables I and II) analogous to those of **1**. The differences in the ^{1}H-NMR coupling patterns of the α- and β-protons in the chalcan moiety suggested **2** to be a configurational isomer of **1**.

When degraded with acid in the presence of benzyl mercaptan, **2** afforded the above-mentioned benzylthioether (**27**) and (−)-epigallocatechin 3-*O*-gallate (**9**), thus confirming the constitution, as well as the *R*-configuration of the β-carbon.



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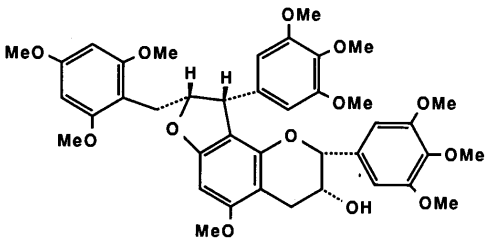

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Chart 4

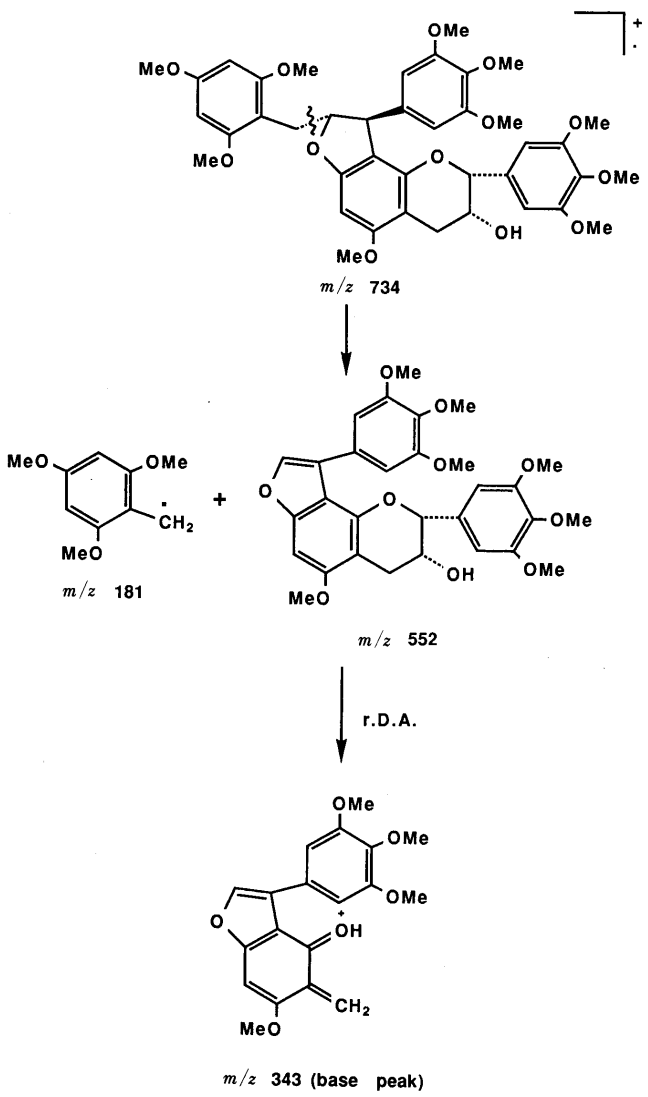


Chart 5. EI-MS Fragmentation Patterns of **28** and **29**

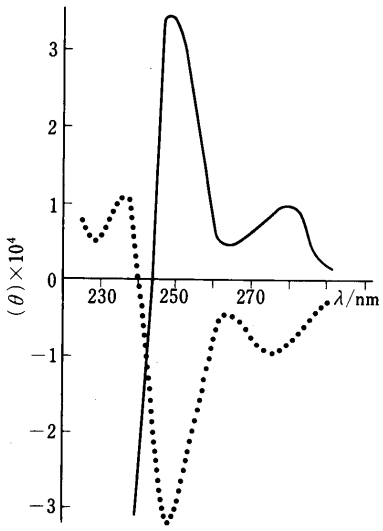
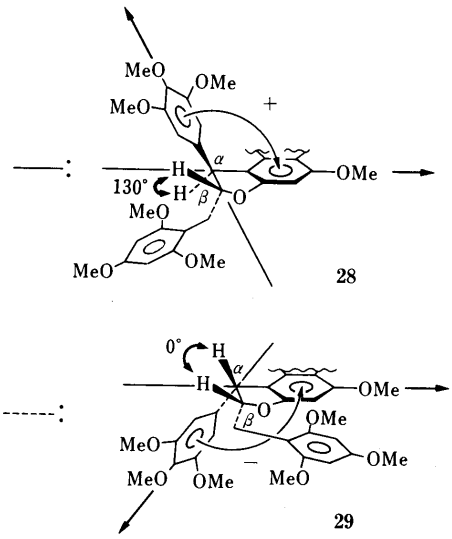


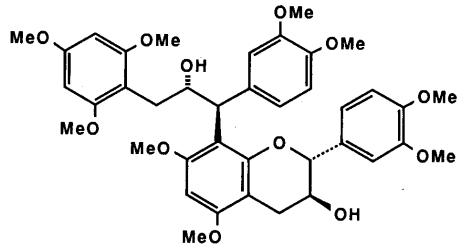
Fig. 1. CD Spectra of **28** and **29**



The chirality of the α-carbon was determined in the same way as in the case of **1**. The undecamethyl ether (**2b**) of the tannase hydrolysate (**2a**) was heated in dry benzene containing *p*-toluenesulfonic acid to yield a dihydrobenzofuran derivative (**29**). The EI-MS of **29** was almost indistinguishable from that of **28**, suggesting that the plane structure is the same. In contrast, the ^{1}H-NMR spectrum of **29** showed the α-methine signal at δ 4.53 with a larger coupling constant of 8.5 Hz. This fact indicated that the dihedral angle between α- and β-protons is *ca.* 0°. Furthermore, a negative Cotton effect at 248 nm (completely opposite to the case in **28**) in the CD spectrum of **29** clearly showed that the α-methine carbon possesses the *R*-configuration (Fig. 1).

The chalcan unit was concluded to be located at the C-8 position of the epigallocatechin moiety, since the ^{13}C-NMR signal patterns of the A-ring in **2b** [δ 89.3 (C-6), 112.2 (C-8) and 101.2 (C-4a)] were almost identical with those found in **1b**.

Assamicain C (**3**) gave, in the FAB-MS, the $(M+H)^+$ peak at *m/z* 917 identical with those of **1** and **2**. The ^{1}H- and ^{13}C-NMR spectra (Tables I and II) were consistent with the chalcan-flavan structure. Thiolytic degradation of **3** afforded the above thioether (**27**) and (−)-epigallocatechin 3-*O*-gallate (**9**), thus establishing unambiguously the absolute stereochemistry of the asymmetric carbons except the α-methine carbon. The absolute configuration of the α-carbon was concluded to be in the *S*-series on the basis of the coupling constant (J=6 Hz) of the α-proton signal, which was similar to that found in **1**.



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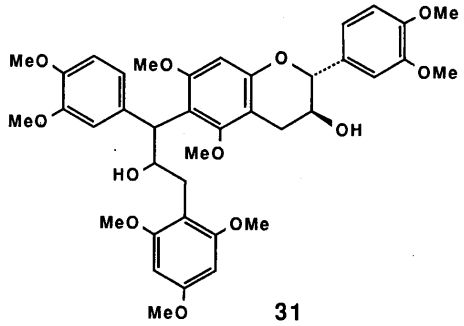

31

Chart 6

The location of the chalcan unit in the epigallocatechin moiety was determined in the same way as described above. The ^{13}C-NMR spectrum of the undecamethyl ether (**3b**) showed the C-6, C-8 and C-4a signals at δ 118.3, 96.8 and 108.6, respectively, the chemical shifts being in good agreement with those of the C-6 substituted catechin derivative, gambiriin A_3 nonamethyl ether (**31**) (*vide ante*).

The structures of assamicains obtained here were further confirmed by synthesis (Chart 7). The benzylthioether (**27**), prepared from (−)-epigallocatechin 3-*O*-gallate (**9**) by acid-catalyzed thiolytic degradation, was treated with acid to generate a carbocation.[14] When (−)-epigallocatechin 3-*O*-gallate (**9**) was present, its A-ring served as a nucleophile to give four condensation products, among which three were found to be identical with assamicains A (**1**), B (**2**) and C (**3**). The structure of the remaining compound (**32**) was concluded to be a configurational isomer of **3** by comparison of its ^{1}H-NMR spectrum with those of **1**, **2** and **3** (Table I).

Compound **14** was a flavan-3-ol derivative as revealed by ^{1}H-NMR examination. The appearance of the flavan H-2 signal (δ 5.04) as a broad singlet suggested the 2,3-*cis* configuration, while a two-proton aromatic resonance at δ 6.61 was consistent with the epigallocatechin structure. The lowfield shift (δ 5.47, m) of the H-3 signal, as well as the observation of aromatic ABX-type signals at δ 6.82 (d, J= 8 Hz), 7.03 (dd, J=2, 8 Hz) and 7.11 (d, J=2 Hz) and mutually coupled *trans*-olefinic signals at δ 6.16 (d, J= 16 Hz) and 7.44 (d, J=16 Hz), suggested the location of a caffeoyl moiety at the C-3 position.

The caffeic acid ester bond was successfully cleaved by enzymatic hydrolysis with tannase, which yielded (−)-epigallocatechin (**6**) and caffeic acid, thus confirming the structure of **14** to be (−)-epigallocatechin 3-*O*-caffeoate.

Compounds **19** and **20** were found to possess the same

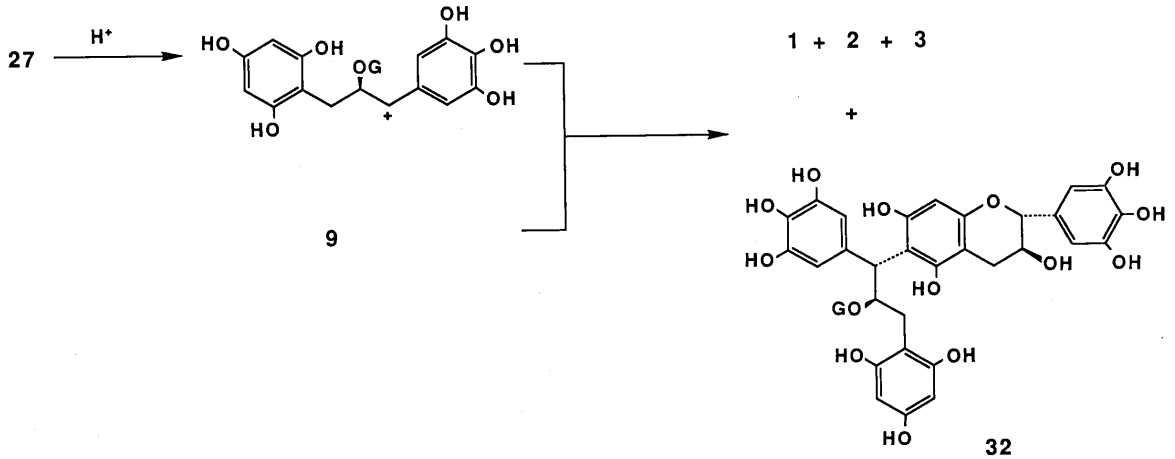

Chart 7

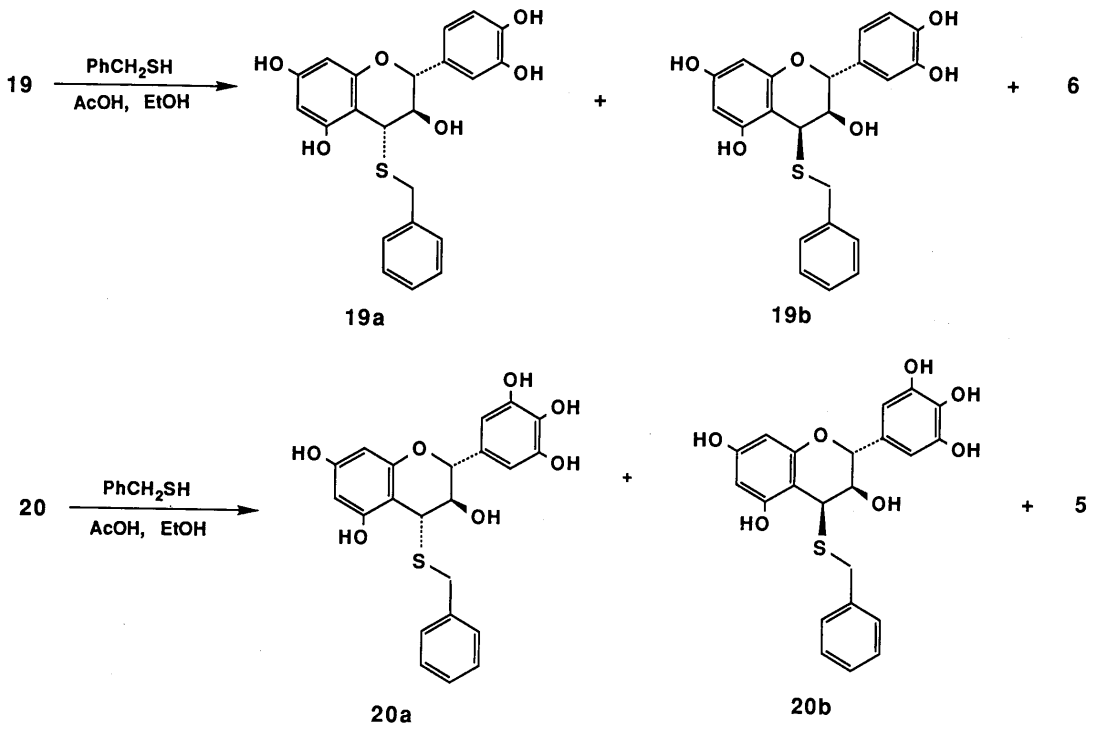

Chart 8

molecular formula by elemental analysis. The ^{1}H-NMR spectra of these compounds were extremely complicated by conformational isomerism,[15] but were similar to that of procyanidin B-4 (**18**), especially in the aliphatic region.

On acid-catalyzed degradation with benzylmercaptan, **19** gave (−)-epigallocatechin (**6**) (formed from the lower unit) and two benzylthioethers (**19a** and **19b**) (from the upper half), the latter two being found to be identical with (+)-catechin 4α- and 4β-benzylthioethers by physical and spectral comparisons.[16] On the other hand, similar thiolytic degradation of **20** furnished (−)-epicatechin (**5**) and (+)-gallocatechin 4α- and 4β-benzylthioethers (**20a** and **20b**).[17]

The location and the mode of the interflavanoid linkage were concluded to be 4α-8 from the similarities of the aliphatic signal patterns with those of **18**, thus characterizing **19** and **20** as catechin-(4α-8)-epigallocatechin and gallocatechin-(4α-8)-epicatechin, respectively.

Assamicains isolated in this study represent the second example of chalcan-flavan dimers.[13] The fact that assamicains are not found in black tea indicated that they are almost completely degraded by endogeneous polyphenol oxidase at the fermentation stage. Furthermore, the absence of these compounds in various green teas and oolong teas so far examined, and even in fresh green tea leaf, implies that they will be useful as markers in the chemotaxonomy of the species of the genus *Camellia*.

Experimental

Details of the instruments and chromatographic conditions used in this study were essentially the same as described in the previous paper.[4]

Extraction and Isolation The fresh leaves of *Camellia sinensis* var. *assamica* (5.0 kg) collected in May 1985 in Ibusuki City, Kagoshima Prefecture, were extracted three times with 80% aqueous acetone at room temperature. The acetone was removed by evaporation under reduced pressure (*ca.* 40 °C), and the resulting aqueous solution afforded dark green precipitates consisting mainly of chlorophylls, which were removed by filtration. The filtrate was applied to a column of Sephadex LH-20, preswollen with H_2O. Elution with H_2O containing increasing amounts of MeOH and finally with 50% aqueous acetone afforded five fractions: I (91 g), II (64 g), III (28 g), IV (80 g) and V (11 g). Fraction I consisted largely of caffeine. Continuous chromatography of frs. II—V on columns of Sephadex LH-20, MCI gel CHP-20P and Bondapak C_{18} Porasil B with various solvent systems as shown in Chart 1 to furnish compounds **1**—**26**.

Assamicain A (1) An off-white amorphous powder, $[\alpha]_D^{17}$ −120.0° (*c* = 1.0, acetone). *Anal.* Calcd for $C_{44}H_{36}O_{22}\cdot 3H_2O$: C, 54.43; H, 4.36. Found: C, 54.67; H, 4.55. FAB-MS *m/z*: 917 [(M+H)$^+$, 17%]. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Assamicain B (2) An off-white amorphous powder, $[\alpha]_D^{17}$ −54.3° (*c* = 1.0, acetone). *Anal.* Calcd for $C_{44}H_{36}O_{22}\cdot 5H_2O$: C, 52.49; H, 4.61. Found: C, 52.98; H, 4.85. FAB-MS *m/z*: 917 [(M+H)$^+$, 12%]. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Assamicain C (3) An off-white amorphous powder, $[\alpha]_D^{17}$ +60.5° (*c* = 1.3, acetone). *Anal.* Calcd for $C_{44}H_{36}O_{22}\cdot 5H_2O$: C, 52.49; H, 4.61. Found: C, 52.20; H, 4.45. FAB-MS *m/z*: 917 [(M+H)$^+$, 8%]. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Thiolytic Degradation of 1—3 and 9 a) A solution of **1** (130 mg) in 0.2 N HCl–EtOH (5 ml) containing toluene-α-thiol (2 ml) was refluxed for 3 h. The reaction mixture was concentrated under reduced pressure to give an oily residue, which was chromatographed over Sephadex LH-20 (EtOH). Rechromatography on a column of Sephadex LH-20 (H_2O–MeOH) afforded **9** (16 mg) and a thioether (**27**) (54 mg) as an off-white amorphous powder, $[\alpha]_D^{24}$ +1.6° (*c* = 0.5, acetone). *Anal.* Calcd for $C_{29}H_{26}O_{11}S\cdot H_2O$: C, 57.99; H, 4.70. Found: C, 57.67; H, 4.79. ^{1}H-NMR (acetone-d_6 + D_2O): 2.77—3.18 (2H, m, γ-H), 3.65 (2H, s, $-SCH_2-$), 3.99 (1H, d, *J* = 5 Hz, α-H), 5.68 (1H, m, β-H), 5.91 (2H, s, 3′,5′-H), 6.53, 6.67 (2H in total, each s, 2,6-H), 7.10—7.32 (7H in total, galloyl H, aromatic H). ^{13}C-NMR (acetone-d_6 + D_2O): 27.0 (γ-C), 36.6 (SCH_2), 55.0 (α-C), 77.0 (β-C), 95.2 (3′,5′-C), 103.0 (1′-C), 108.6 (2,6-C), 110.2 (galloyl 2,6-C), 122.1 (galloyl 1-C), 127.5 (aromatic 4-C), 129.1 (aromatic 3,5-C), 129.9 (aromatic 2,6-C), 131.8, 132.8 (1,4-C), 138.7 (aromatic 1-C), 139.1 (galloyl 4-C), 145.7, 146.3 (3,5-C, galloyl 3,5-C), 154.7 (4′-C), 157.9 (2′,6′-C), 167.0 (–COO–).

b) A solution of **2** (50 mg) in 0.2 N HCl–EtOH (3 ml) containing toluene-α-thiol (1 ml) was heated under reflux for 3 h. Work-up as described above yielded **9** (7 mg) and **27** (23 mg).

c) A mixture of **3** (55 mg) and toluene-α-thiol (1 ml) in 0.2 N HCl–EtOH (4 ml) was treated as described above to give **9** (3 mg) and **27** (8 mg).

d) A mixture of **9** (1 g) and toluene-α-thiol (10 ml) in 0.5 N HCl–EtOH (50 ml) was refluxed for 8 h. The reaction mixture was concentrated under

reduced pressure, and an oily residue was chromatographed over Sephadex LH-20 (EtOH) to give **27** (629 mg).

Methylation of 27 A mixture of **27** (45 mg), Me_2SO_4 (0.3 ml) and anhydrous K_2CO_3 (0.3 g) in dry acetone (7 ml) was refluxed for 2 h with stirring. After removal of inorganic salts by filtration, the filtrate was concentrated to a syrup, which was chromatographed over silica gel. Elution with hexane–EtOAc (3 : 1, v/v) yielded a nonamethyl ether (**27a**) (28 mg) and (−)-gallocatechin 3-*O*-gallate octamethyl ether (**27b**) (7 mg). **27a**: Colorless needles (*n*-hexane–$CHCl_3$–MeOH), mp 99—100 °C, $[\alpha]_D^{17}$ +5.3° (*c*=0.5, acetone). *Anal.* Calcd for $C_{38}H_{44}O_{15}S$: C, 64.39; H, 6.26. Found: C, 64.11; H, 6.24. EI-MS *m/z*: 617 $(M-PhCH_2)^+$, 585 $(M-PhCH_2S)^+$. ^{1}H-NMR ($CDCl_3$): 2.75—3.16 (2H, m, γ-H), 3.55—3.98 (28H, m, 9×OCH_3, β-H), 5.73 (1H, m, α-H), 5.79 (1H, s, 3′,5′-H), 6.52, 6.63 (2H in total, each s, 2,6-H), 7.11—7.28 (7H, m, aromatic H, galloyl H). **27b**: Colorless granules (*n*-hexane–$CHCl_3$–MeOH), mp 127—130 °C, $[\alpha]_D^{18}$ −47.6° (*c*=0.3, acetone). ^{1}H-NMR ($CDCl_3$): 2.79 (1H, dd, *J*=16, 7 Hz, 4-H), 3.17 (1H, dd, *J*=16, 5 Hz, 4-H), 3.78—3.90 (24H, 8×OCH_3), 5.10 (1H, d, *J*=7 Hz, 2-H), 5.50 (1H, dt, *J*=5, 7 Hz, 3-H), 6.12, 6.21 (each 1H, d, *J*=2 Hz, 6,8-H), 6.66 (2H, s, 2′,6′-H), 7.12 (2H, s, galloyl H). Methylation of (+)-gallocatechin 3-*O*-gallate (20 mg) with Me_2SO_4 (0.2 ml) and anhydrous K_2CO_3 (0.2 g) in dry acetone (3 ml) yielded the octamethyl ether (25 mg) as colorless granules (*n*-hexane–$CHCl_3$–MeOH), mp 115—117 °C, $[\alpha]_D^{20}$ +68.4° (*c*=1.0, acetone). The ^{1}H-NMR spectrum was identical with that of **27b**.

Enzymatic Hydrolysis of 1—3 with Tannase Solutions of **1** (120 mg), **2** (260 mg) and **3** (60 mg) in H_2O (5—10 ml) were each shaken with tannase at room temperature for 10 min. The reaction mixture was concentrated under reduced pressure and the residue was treated with EtOH. The insoluble materials were removed by filtration, and the filtrate was applied to a Sephadex LH-20 column. Elution with EtOH yielded gallic acid, **1a** (50 mg), **2a** (120 mg) and **3a** (20 mg). **1a**: An off-white amorphous powder, $[\alpha]_D^{14}$ −76.1° (*c*=1.0, acetone). *Anal.* Calcd for $C_{30}H_{28}O_{14}\cdot 3H_2O$: C, 54.05; H, 5.14. Found: C, 54.05; H, 5.11. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. **2a**: An off-white amorphous powder, $[\alpha]_D^{17}$ −55.6° (*c*=1.0, acetone). *Anal.* Calcd for $C_{30}H_{28}O_{14}\cdot 5/2H_2O$: C, 54.79; H, 5.06. Found: C, 55.01; H, 5.44. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. **3a**: Colorless needles, mp 223—225 °C, $[\alpha]_D^{20}$ +29.4° (*c*=1.3, acetone). *Anal.* Calcd for $C_{30}H_{28}O_{14}\cdot 4H_2O$: C, 52.63; H, 5.30. Found: C, 52.30; H, 5.26. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Methylation of 1, 2, 1a, 2a and 3a Solutions of **1** (30 mg), **2** (30 mg), **1a** (45 mg), **2a** (100 mg) and **3a** (20 mg) in dry acetone containing Me_2SO_4 (0.2—0.5 ml) and anhydrous K_2CO_3 (0.3—1.0 g) were each treated as above. Silica gel column chromatography with benzene–acetone (9 : 1 and 3 : 1, v/v) yielded **1c** (22 mg), **2c** (21 mg), **1b** (22 mg), **2b** (50 mg) and **3b** (7 mg). **1c**: An off-white amorphous powder, $[\alpha]_D^{24}$ −107.3° (*c*=0.5, acetone). *Anal.* Calcd for $C_{61}H_{70}O_{22}\cdot H_2O$: C, 62.45; H, 6.18. Found: C, 62.84; H, 6.28. EI-MS *m/z*: 942 (M − trimethoxybenzoyl)$^+$, 730 (M − 2×trimethoxybenzoyl)$^+$. ^{1}H-NMR ($CDCl_3$): 2.80—3.10 (4H, m, γ-H, flavan 4-H), 3.54—3.80 (OCH_3), 5.04 (1H, d, *J*=10 Hz, α-H), 5.05 (1H, s, flavan 2-H), 5.56—5.74 (2H, m, β-H, flavan 3-H), 5.92 (2H, s, 3′,5′-H), 5.94 (1H, s, flavan 6-H), 6.72, 6.79 (each 2H, br s, 2,6-H, flavan 2′,6′-H), 6.85, 7.19 (each 2H, br s, galloyl H). ^{13}C-NMR: Table II. **2c**: An off-white amorphous powder, $[\alpha]_D^{24}$ −183.6° (*c*=0.5, acetone). *Anal.* Calcd for $C_{61}H_{70}O_{22}\cdot H_2O$: C, 62.45; H, 6.18. Found: C, 62.93; H, 6.24. EI-MS *m/z*: 942 (M − trimethoxybenzoyl)$^+$, 730 (M − 2×trimethoxybenzoyl)$^+$. ^{1}H-NMR ($CDCl_3$): 2.84—3.20 (4H, m, γ-H, flavan 4-H), 3.49—3.94 (OCH_3), 4.90 (1H, br d, *J*=8 Hz, α-H), 5.30 (1H, br s, flavan 2-H), 5.75 (2H, m, β-H, flavan 3-H), 5.95 (2H, s, 3′,5′-H), 6.19 (1H, s, flavan 6-H), 6.50—7.20 (8H in total, m, 2,6-H, flavan 2′,6′-H, 2×galloyl H). ^{13}C-NMR: Table II. **1b**: An off-white amorphous powder, $[\alpha]_D^{18}$ +66.7° (*c*=0.2, acetone). *Anal.* Calcd for $C_{41}H_{50}O_{14}\cdot 1/2H_2O$: C, 63.47; H, 6.63. Found: C, 63.72; H, 6.96. EI-MS *m/z*: 766 (M^+). ^{1}H-NMR ($CDCl_3$): 2.58 (1H, dd, *J*=13, 8 Hz, γ-H), 2.87 (1H, dd, *J*=13, 3 Hz, γ-H), 2.93 (2H, m, flavan 4-H), 3.62—3.87 (OCH_3), 4.35 (1H, m, flavan 3-H), 4.65 (1H, d, *J*=10 Hz, α-H), 4.81 (1H, m, β-H), 4.90 (1H, br s, flavan 2-H), 6.09 (2H, s, 3′,5′-H), 6.18 (1H, s, flavan 6-H), 6.73 (2H, s, 2,6-H), 6.83 (2H, br s, flavan 2′,6′-H). ^{13}C-NMR: Table II. **2b**: An off-white amorphous powder, $[\alpha]_D^{24}$ +79.7° (*c*=0.7, acetone). *Anal.* Calcd for $C_{41}H_{50}O_{14}$: C, 64.22; H, 6.57. Found: C, 64.05; H, 6.74. EI-MS *m/z*: 766 (M^+). ^{1}H-NMR ($CDCl_3$): 2.65 (1H, dd, *J*=13, 8 Hz, γ-H), 2.93 (2H, m, flavan 4-H), 2.96 (1H, br d, *J*=13 Hz, γ-H), 3.69—3.98 (OCH_3), 4.12 (1H, m, flavan 3-H), 5.27 (1H, m, β-H), 6.17 (2H, s, 3′,5′-H), 6.23 (1H, s, flavan 6-H), 6.67, 6.71 (each 2H, s, 2,6-H, flavan 2′,6′-H). ^{13}C-NMR: Table II. **3b**: An off-white amorphous powder, $[\alpha]_D^{18}$ 0° (*c*=0.7, $CHCl_3$). *Anal.* Calcd for $C_{41}H_{50}O_{14}\cdot 3/2H_2O$: C, 62.02; H, 6.73. Found: C, 62.24; H, 6.62. EI-MS *m/z*: (M^+). ^{1}H-NMR ($CDCl_3$): 2.67 (1H, dd, *J*=14, 9 Hz, γ-H), 2.99 (1H, dd, *J*=14, 3 Hz, γ-H), 3.07 (2H, m, flavan 4-H), 3.73—3.87 (OCH_3), 4.25 (1H, m, β-H), 4.93 (1H, br s, flavan 2-H), 6.13 (2H, s, 3′,5′-H), 6.38 (1H, s, flavan 8-H), 6.71, 6.79 (each 2H, s, 2,6-H, flavan 2′,6′-H). ^{13}C-NMR: Table II.

Acid Treatment of 1b and 2b Solutions of **1b** (10 mg) and **2b** (30 mg) in dry benzene (5 and 15 ml) containing *p*-toluenesulfonic acid (3 and 15 mg) were each refluxed for 0.5 h. After cooling, the reaction mixture was separated by preparative thin layer chromatography (TLC) [silica gel, 0.25 mm thick, $CHCl_3$–EtOAc (30 : 1, v/v)] and silica gel column chromatography [*n*-hexane–EtOAc (1 : 1—1 : 2)] to yield **28** (7 mg) and **29** (3 mg). **28**: An off-white amorphous powder, $[\alpha]_D^{17}$ −109.4° (*c*=0.7, acetone). *Anal.* Calcd for $C_{40}H_{46}O_{13}$: C, 65.38; H, 6.31. Found: C, 65.03; H, 6.40. EI-MS *m/z*: 734 (M^+), 552, 343, 181. ^{1}H-NMR ($CDCl_3$): 2.93 (2H, m, flavan 4-H), 3.09 (2H, m, γ-H), 3.54—3.83 (OCH_3), 4.39 (1H, d, *J*=3.9 Hz, α-H), 4.41 (1H, m, flavan 3-H), 4.86 (1H, br s, flavan 2-H), 4.90 (1H, m, β-H), 6.03 (2H, s, 3′,5′-H), 6.15 (2H, s, 2,6-H), 6.17 (1H, s, flavan 6-H), 6.56 (2H, s, flavan B-ring H). CD (*c*=3.0×10^{-5}, MeOH) $[\theta]^{23}$ (nm): −134000 (231), 34400 (248), 980 (280). **29**: An off-white amorphous powder, $[\alpha]_D^{17}$ +10.9° (*c*=0.2, acetone). EI-MS *m/z*: 734 (M^+), 552, 343, 181. ^{1}H-NMR ($CDCl_3$): 2.54—2.77 (2H, m, γ-H), 2.94 (2H, m, flavan 4-H), 3.66—3.83 (OCH_3), 4.19 (1H, m, flavan 3-H), 4.53 (1H, d, *J*=8.5 Hz, α-H), 4.93 (1H, br s, flavan 2-H), 5.30 (1H, m, β-H), 6.10 (2H, s, 3′,5′-H), 6.15 (1H, s, flavan 6-H), 6.34 (4H, s, 2,6-H, flavan B-ring H). CD (*c*=3.0×10^{-5}, MeOH) $[\theta]^{23}$ (nm): 10600 (231), −32400 (248), −9900 (275).

Synthesis of Assamicains A mixture of **9** (5 g) and **27** (1 g) in 0.01 N HCl–EtOH (20 ml) was refluxed for 12 h. After cooling, the reaction mixture was directly chromatographed on a column of Sephadex LH-20 (EtOH). Rechromatography on columns of Fuji gel ODS G3 and Bondapak C_{18}/Porasil B (H_2O–MeOH) yielded **1** (163 mg), **2** (67 mg), **3** (37 mg) and **32** (4 mg). **32**: A tan amorphous powder, $[\alpha]_D^{19}$ +17.0° (*c*=0.4, acetone). ^{1}H-NMR: Table I.

(−)-Epigallocatechin 3-*O*-Caffeoate (14) An off-white amorphous powder, $[\alpha]_D^{28}$ −160.5° (*c*=0.4, acetone). *Anal.* Calcd for $C_{24}H_{20}O_{10}\cdot 3/2H_2O$: C, 58.18; H, 4.68. Found: C, 58.19; H, 4.55. FD-MS *m/z*: 469 $(M+H)^+$, 306 (epigallocatechin)$^+$, 180 (caffeic acid)$^+$. ^{1}H-NMR (acetone-d_6): 2.87 (1H, dd, *J*=14, 8 Hz, 4-H), 3.08 (1H, dd, *J*=14, 5 Hz, 4-H), 5.04 (1H, br s, 2-H), 5.47 (1H, m, 3-H), 6.02, 6.07 (each 1H, s, *J*=2 Hz, 6,8-H), 6.16 (1H, d, *J*=16 Hz, olefinic α-H), 6.61 (2H, s, 2′,6′-H), 6.82 (1H, d, *J*=8 Hz, caffeoyl 5-H), 7.03 (1H, dd, *J*=8, 2 Hz, caffeoyl 6-H), 7.11 (1H, d, caffeoyl 2-H), 7.44 (1H, d, *J*=16 Hz, olefinic β-H). ^{13}C-NMR (acetone-d_6): 26.4 (4-C), 69.0 (3-C), 77.9 (2-C), 95.8, 96.4 (6,8-C), 98.9 (4a-C), 106.8 (2′,6′-C), 115.1, 116.2 (caffeoyl 2,5-C), 115.4 (olefinic α-C), 122.6 (caffeoyl 6-C), 127.5 (caffeoyl 1-C), 130.6 (1′-C), 133.4 (4′-C), 146.1, 146.3 (3′,5′-C, caffeoyl 3,4-C), 148.8 (olefinic β-C), 156.9, 157.4, 157.8 (5, 7, 8a-C), 167.0 (–COO–).

Tannase Hydrolysis of 14 A solution of **14** (1 mg) in H_2O (2 ml) was shaken with tannase at room temperature for 2 h. Caffeic acid and (−)-epigallocatechin were detected by TLC, caffeic acid: silica gel G, benzene–HCOOEt–HCOOH (5 : 4 : 1, v/v), *Rf* 0.50; benzene–acetone (2 : 1, v/v), *Rf* 0.14. (−)-epigallocatechin: silica gel G, benzene–HCOOEt–HCOOH (3 : 6 : 1, v/v), *Rf* 0.41, Cellulose, 2% AcOH, *Rf* 0.15.

Catechin-(4α-8)-epigallocatechin (19) A tan amorphous powder, $[\alpha]_D^{17}$ −168.9° (*c*=1.0, acetone). *Anal.* Calcd for $C_{30}H_{26}O_{13}\cdot 3/2H_2O$: C, 57.97; H, 4.70. Found: C, 58.36; H, 4.75. ^{1}H-NMR (acetone-d_6+D_2O): 2.53—3.00 (2H, m, 4′-H), 3.33—5.00 (5H in total, m, 2,3,4,2′,3′-H), 5.86—6.40 (3H in total, m, 6,8,6′-H), 6.59—7.28 (5H in total, m, B,B′-ring H). ^{13}C-NMR (acetone-d_6+D_2O): 29.6 (4′-C), 38.3 (4-C), 66.9 (3′-C), 73.2 (3-C), 80.0 (2′-C), 83.4 (2-C), 96.2, 97.3, 97.7 (6,8,6′-C), 99.7 (4a′-C), 106.8 (B′-ring 2,6-C), 107.8, 108.1 (4a, 8′-C), 115.6, 116.0 (B-ring 2,5-C), 120.9 (B-ring 6-C), 131.3, 132.4 (B,B′-ring 1-C), 133.0 (B′-ring 4-C), 145.4, 145.7, 145.8, 146.2 (B-ring 3,4-C, B′-ring 3,5-C), 154.9, 155.3, 156.0, 156.7, 157.2 (5,7,8a,5′,7′,8a′-C).

Gallocatechin-(4α-8)-epicatechin (20) A tan amorphous powder, $[\alpha]_D^{17}$ −216.4° (*c*=1.0, acetone). *Anal.* Calcd for $C_{30}H_{26}O_{13}\cdot 3/2H_2O$: C, 57.97; H, 4.70. Found: C, 58.33; H, 4.72. ^{1}H-NMR (acetone-d_6+D_2O): 2.52—3.00 (2H, m, 4′-H), 3.70—5.00 (5H in total, m, 2,3,4,2′,3′-H), 5.82—6.20 (3H in total, m, 6,8,6′-H), 6.38—7.25 (5H in total, m, B,B′-ring H). ^{13}C-NMR (acetone-d_6+D_2O): 29.6 (4′-C), 38.1 (4-C), 66.9 (3′-C), 73.2 (3-C), 79.9 (2′-C), 83.5 (2-C), 96.2, 97.3, 97.6 (6,8,6′-C), 99.5 (4a′-C), 108.1 (B-ring 2,6-C), 106.0, 107.7 (4a, 8′-C), 115.1, 115.6 (B′-ring 2,5-C), 119.0 (B′-ring 6-C), 131.6, 131.8 (B,B′-ring 1-C), 133.4 (B-ring 4-C), 145.3, 145.4, 145.9, 146.6 (B′-ring 3,4-C, B-ring 3,5-C), 154.9, 155.3, 156.0, 157.1, 157.4, 158.3 (5,7,8a,5′,7′,8a′-C).

Thiolytic Degradation of 19 and 20 Solutions of **19** (30 mg) and **20** (30 mg) in EtOH (3 ml) containing AcOH (0.5 ml) and toluene-α-thiol

(1 ml) were each refluxed for 5 h. After cooling, the reaction mixture was concentrated under reduced pressure to give an oily residue, which was chromatographed over Sephadex LH-20 [$CHCl_3$–EtOH (3 : 1—0 : 1), v/v] to yield **6** (3 mg), **19a** (1 mg) and **19b** (7 mg) (from **19**) and **5** (9 mg), **20a** (4 mg) and **20b** (1 mg) (from **20**). **19a**: An off-white amorphous powder, $[\alpha]_D^{14}$ +32.3° (c=0.1, acetone). ^{1}H-NMR (acetone-d_6+D_2O): 3.76, 3.95 (each 1H, d, J=12 Hz, –SCH_2–), 4.00 (1H, d, J=7 Hz, 4-H), 4.15 (1H, br t, J=7 Hz, 3-H), 4.49 (1H, d, J=7 Hz, 2-H), 5.96, 6.07 (each 1H, d, J=2 Hz, 6,8-H), 6.73 (1H, dd, J=8, 2 Hz, 6′-H), 6.82 (1H, d, J=8 Hz, 5′-H), 6.90 (1H, d, J=2 Hz, 2′-H), 7.22—7.44 (5H in total, m, aromatic H). **19b**: An off-white amorphous powder, $[\alpha]_D^{14}$ +28.0° (c=0.7, acetone). ^{1}H-NMR (acetone-d_6+D_2O): 4.09 (2H, s, –SCH_2–), 4.12 (1H, dd, J=10, 4 Hz, 3-H), 4.38 (1H, d, J=4 Hz, 4-H), 4.94 (1H, d, J=10 Hz, 2-H), 5.82, 6.03 (each 1H, d, J=2 Hz, 6,8-H), 6.76 (1H, dd, J=8, 2 Hz, 6′-H), 6.84 (1H, d, J=8 Hz, 5′-H), 6.93 (1H, br s, 2′-H), 7.16—7.46 (5H in total, m, aromatic H). **20a**: An off-white amorphous powder, $[\alpha]_D^{14}$ +29.3° (c=0.4, acetone). ^{1}H-NMR (acetone-d_6+D_2O): 3.77, 3.95 (each 1H, d, J=10 Hz, –SCH_2–), 3.94 (1H, d, J=6 Hz, 4-H), 4.18 (1H, br t, J=7 Hz, 3-H), 4.41 (1H, d, J=7 Hz, 2-H), 5.95, 6.06 (each 1H, d, J=2 Hz, 6,8-H), 6.47 (2H, s, 2′,6′-H), 7.20—7.39 (5H in total, m, aromatic H). **20b**: An off-white amorphous powder, $[\alpha]_D^{14}$ +7.3° (c=1.1, acetone). ^{1}H-NMR (acetone-d_6+D_2O): 4.07 (2H, s, –SCH_2–), 4.13 (1H, dd, J=10, 5 Hz, 3-H), 4.38 (1H, d, J=5 Hz, 4-H), 4.87 (1H, d, J=10 Hz, 2-H), 5.80, 6.04 (each 1H, d, J=2 Hz, 6,8-H), 6.51 (2H, s, 2′,6′-H), 7.15—7.48 (5H in total, m, aromatic H).

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